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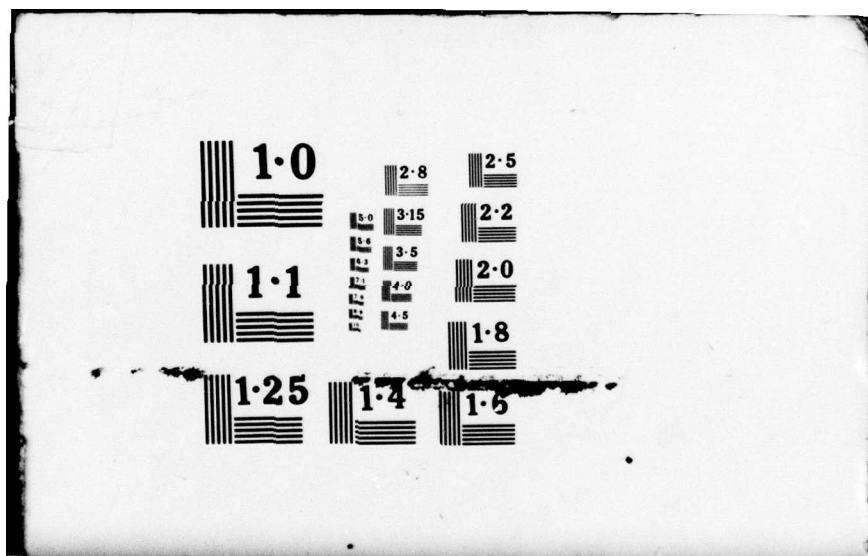
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# DEFENCE RESEARCH ESTABLISHMENT OTTAWA

DREO TECHNICAL NOTE NO. 78-19

DREO-TN-78-19

THE ELECTRICAL CONDUCTIVITY OF  
 $\text{Li}_2\text{SO}_4$ :  $\text{LiBr}$ : 0.07  $\text{K}_2\text{SO}_4$ .

by  
Arthur W. Johnson



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THE ELECTRICAL CONDUCTIVITY OF  $\text{Li}_2\text{SO}_4:\text{LiBr}:0.07 \text{ K}_2\text{SO}_4$

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A.W. Johnson

Energy Conversion Division

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ABSTRACT

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A lithium sulphate-based solid electrolyte has been synthesized, incorporating lithium bromide and potassium sulphate, which exhibits a transition to a highly conducting phase at 312°C. The new phase extends to 559°C, the melting point of the compound. At 326°C,  $\sigma = 0.08 \Omega^{-1} \text{cm}^{-1}$ .

←  $\sigma = 1/0.08 \text{ ohm cm}$

RÉSUMÉ

On a synthétisé un électrolyte solide à base de sulfate de lithium en combinant du bromure de lithium et du sulfate de potassium; il présente une transition à 312°C qui correspond à une phase très conductive persistant jusqu'à 559°C, le point de fusion du composé. A 326°C,  $\sigma = 0.08 \Omega^{-1} \text{cm}^{-1}$ .

## INTRODUCTION

Electrochemical systems employing solid electrolytes present many advantages compared to devices using liquid electrolytes. These include the elimination of gassing and leakage, reduction in corrosion, operation over a wide temperature range, long shelf life, relative immunity to shock and vibration, possibility of hermetic sealing and producibility in almost any shape. Depending upon the ultimate use, the electrolyte may be in the form of a solid, a flexible polymer or a thin film. These electrolytes may be employed in batteries and coulometers in fuze applications, "keep-alive" power sources in printed circuits, state-of-charge indicators for larger batteries, timing circuits and high value capacitors. The disadvantages of such systems are the low current density, possible susceptibility to moisture and, with silver-based electrolytes especially, low terminal voltage ( $\leq 0.67$  V).

The low limiting current density of solid electrolyte cells results from the low conduction of the electrolyte and polarization at the electrode-electrolyte interface. The electrode contact problem may be alleviated in compressed powder electrolytes by amalgamating the surface layer of the electrolyte or, preferably, by pressing into the surface of the pellet at the time of compaction a mixture of solid electrolyte and powdered electrode material. This mixed electrolyte-electrode concept is analogous to the use of porous electrodes in liquid electrolyte cells to increase the interfacial area and decrease the local current density. Amalgamation is not generally satisfactory because the mercury may react with the electrolyte.

Factors influencing the conductivity of solid electrolytes include the mobility of the conducting ion and the number of available sites for it in the crystal lattice. Certain structures, such as the tetrahedral geometry in bcc and fcc materials provide many possible sites over which the cations may be distributed. Such structures also contain channels through which the ions can migrate easily. At high temperatures, an increase in lattice defects provides more sites and conducting ions, such as in the conducting oxides which become useful as electrolytes only above  $-500^{\circ}\text{C}$ . High room temperature conductivity is obtained in materials with a high degree of cation disorder, as in many AgI-based solid electrolytes.  $\text{RbAg}_4\text{I}_5$ , the solid electrolyte with the highest room temperature conductivity ( $0.27 \Omega^{-1}\text{cm}^{-1}$ ), contains 56 sites per unit cell for the  $\text{Ag}^+$  ions. This material disproportionates slowly at  $27^{\circ}\text{C}$  however, and, like the other silver-bearing solid electrolytes is an expensive product.



Lithium salts, on the other hand, are not only less costly, but they also yield terminal voltages  $>2$  V in certain electrochemical cells. One of the earliest lithium compounds to be investigated is LiI which has been studied extensively by Liang (1). It has been used alone, in combination with  $\text{Al}_2\text{O}_3$  and with  $\text{PbI}_2$ , Pb cathodes. At room temperature, the conductivity of LiI ( $\text{Al}_2\text{O}_3$ ) is reported to be  $10^{-5} \Omega^{-1}\text{cm}^{-1}$  which, however, is only marginally acceptable for thin film cells and is too low for compressed powder cells. Lithium silicates and aluminosilicates provide usable conductivity at high temperatures ( $T > 400^\circ\text{C}$ ), but at  $25^\circ\text{C}$ ,  $\sigma < 10^{-5} \Omega^{-1}\text{cm}^{-1}$  (2). Of greater promise is lithium sulphate. At  $572^\circ\text{C}$  it undergoes a structural change from the  $\beta$ -phase to the fcc  $\alpha$ -phase and the conductivity increases by several orders of magnitude to  $0.8 \Omega^{-1}\text{cm}^{-1}$  (3). This high conductivity phase has been extended to lower temperatures by the addition of suitable ions to form binary or tertiary compounds with reduced transition temperatures. When lithium sulphate is combined with sodium sulphate, the transition temperature,  $T_c$ , of the resultant compound is  $518^\circ\text{C}$ ; if silver sulphate is used,  $T_c = 415^\circ\text{C}$  (4). The divalent ions of magnesium and zinc have also been used to form all-sulphate solid electrolytes (5). Mixed sulphate-halide compounds incorporating LiCl or LiBr with  $\text{Li}_2\text{SO}_4$  have been successfully produced with resultant transition temperatures as low as  $-400^\circ\text{C}$  (6). Adding both  $\text{Na}_2\text{SO}_4$  and  $\text{ZnSO}_4$  to  $\text{Li}_2\text{SO}_4$  yields a ternary compound with  $T_c = 325^\circ\text{C}$  and  $\sigma = 0.1 \Omega^{-1}\text{cm}^{-1}$  (5).  $\text{Na}^+$  and  $\text{Zn}^{2+}$  are small ions ( $0.97 \text{ \AA}$  and  $0.74 \text{ \AA}$  radius respectively) and can substitute for  $\text{Li}^+$  ( $0.68 \text{ \AA}$ ) in the crystal lattice. Larger ions such as  $\text{K}^+$ , with ionic radius  $1.33 \text{ \AA}$ , cannot enter the lattice but are believed to be attracted by dislocations in the salt. These ions will be very mobile along grain boundaries and should contribute to the conductivity even though their solubility is low (4,7).

In this report, the preparation and testing of ternary compounds consisting of  $\text{Li}_2\text{SO}_4$ , LiBr and  $\text{K}_2\text{SO}_4$  are described. They were synthesized with the object of producing an inexpensive solid electrolyte with reduced transition temperature and high conductivity.

#### EXPERIMENTAL

Powdered reagent-grade  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  was dried by heating to the melting point in an alumina crucible and cooling to room temperature. The fused mass was ground by hand and stored in a stoppered bottle. The dehydrated salt absorbs water at very low rate and may be stored without undue precaution (6). Reagent-grade powdered  $\text{K}_2\text{SO}_4$  and anhydrous KBr were used without further purification.



Equi-molar mixtures of  $\text{Li}_2\text{SO}_4$  and  $\text{LiBr}$  plus  $\text{K}_2\text{SO}_4$  in concentrations varying from 0-10 mole percent were ground by hand and dried overnight under vacuum. A drying temperature of  $175^\circ\text{C}$  was used as differential scanning calorimetry indicated that residual water vapour was evolved at  $159^\circ\text{C}$ . The dried powders were transferred to a nitrogen-filled glove box, re-ground, mixed and then pressed at 10 tonnes. The resulting pellet, measuring 12 mm in diameter and about 2 mm thick, was heated to  $475^\circ\text{C}$  for 4 h over 40 Torr of nitrogen in a Pyrex vessel. The effect on the conductivity of sintering for longer periods and under vacuum or over nitrogen or argon at different pressures was also determined. After heating, the pellet was quickly cooled to room temperature, ground in the glove box and pressed at 3 tonnes. Conductivity measurements were made with plane platinum electrodes under light spring pressure and a General Radio 1656 impedance bridge operating at 1 kHz and employing external capacitance compensation. Canox pre-purified nitrogen cover gas was employed during all measurements.

### RESULTS AND DISCUSSION

The variation of the conductivity of  $\text{Li}_2\text{SO}_4:\text{LiBr}:0.07 \text{ K}_2\text{SO}_4$  with temperature is shown in Fig. 1. It can be seen that the conductivity rises rapidly at low temperature and then increases by about three orders of magnitude when the material undergoes a phase transition centred at  $312^\circ\text{C}$ . This transition is about  $30^\circ\text{C}$  wide and leads to a high conductivity phase which extends for more than  $100^\circ\text{C}$ . At  $326^\circ\text{C}$ ,  $\sigma = 0.08 \Omega^{-1}\text{cm}^{-1}$ , rising to  $0.12 \Omega^{-1}\text{cm}^{-1}$  at  $407^\circ\text{C}$ . Above  $415^\circ\text{C}$  the material flowed under slight pressure making measurements unreliable. Differential scanning calorimetric analysis of the compound indicated a single broad peak at the transition temperature and melting at  $559^\circ\text{C}$ . The absence of other peaks suggests that the high temperature phase continues to the melting point. No evidence was found of the  $\beta \rightarrow \alpha$  transition in  $\text{Li}_2\text{SO}_4$  or of the melting of  $\text{LiBr}$  ( $550^\circ\text{C}$ ).

The activation energy for conduction corresponding to the high temperature phase, obtained from the slope of the graph, is 0.17 eV or 3.9 kcal/mole. This figure, which may be compared to 0.14 eV for  $\text{RbAg}_4\text{I}_5$ , indicates high ionic mobility in this temperature range. By contrast, the  $\beta$ -phase activation energies for  $\text{LiBr}$  and  $\text{Li}_2\text{SO}_4$  are 1.22 and 0.36 eV respectively (8).

Similar results were obtained with  $\text{Li}_2\text{SO}_4:\text{LiBr}:x\text{K}_2\text{SO}_4$  for  $0.02 \leq x \leq 0.1$ . The transition temperature remained unchanged and the conductivity in the high temperature phase varied by less than 50%. The small effect on the conductivity and the insensitivity of the transition temperature on the  $\text{K}^+$  ion concentration are to be expected in view of the low solubility of

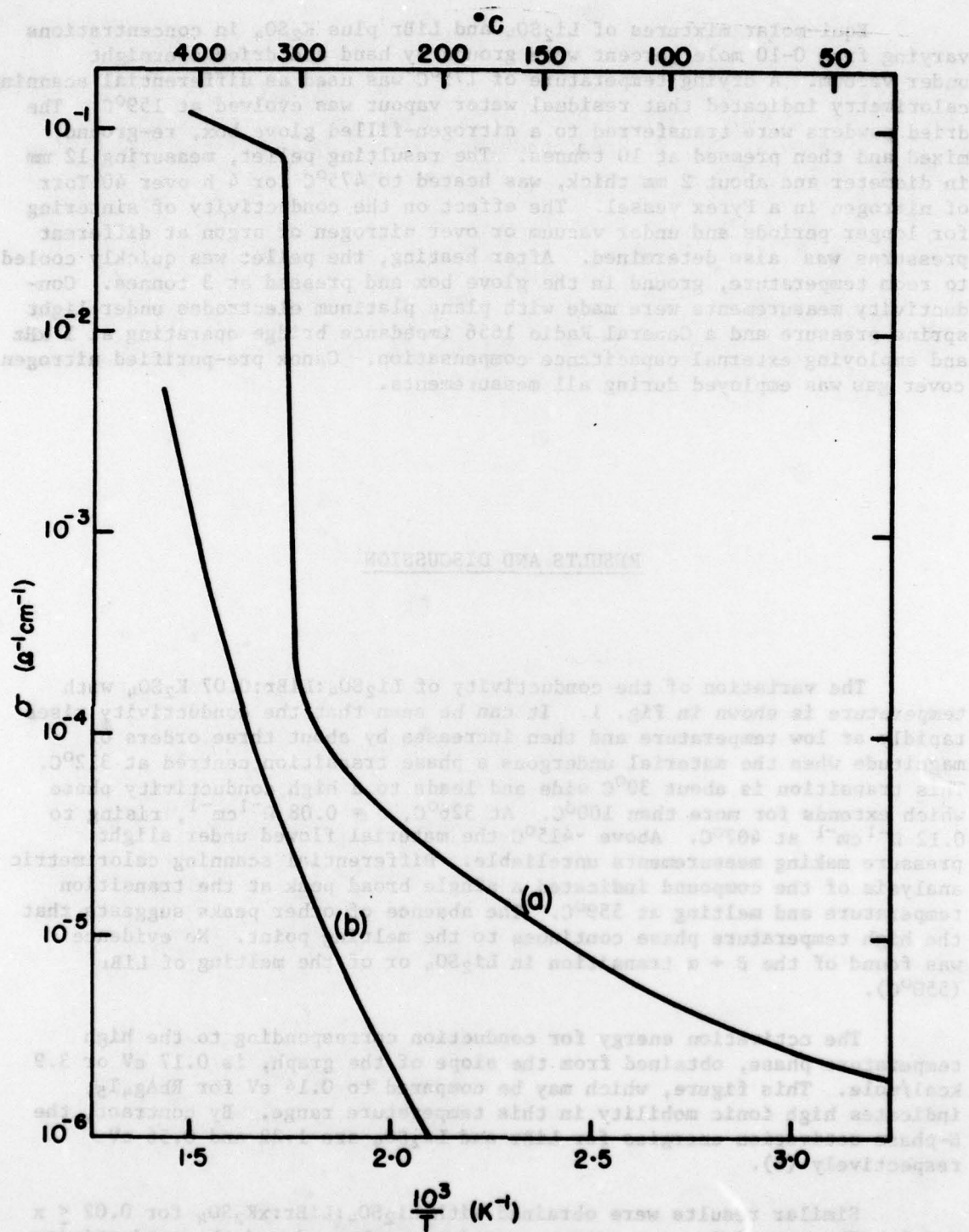


FIGURE 1: Log total conductivity of  $\text{Li}_2\text{SO}_4:\text{LiBr}:x\text{K}_2\text{SO}_4$  as a function of inverse temperature (a)  $x = 0.07$ , (b)  $x = 0$ .

potassium in  $\text{Li}_2\text{SO}_4$ . In all cases, annealing at  $400^\circ\text{C}$  for about two hours was necessary to achieve maximum conductivity. This procedure was required regardless of the length of the sintering phase which was varied from 1 h to 16 h (overnight). Optimum results were obtained with  $\sim 40$  Torr  $\text{N}_2$  or Ar cover gas for both sintering and annealing; results were poorest under vacuum. The compounds exhibiting maximum conductivity were dull grey in colour and all were hygroscopic.

In the binary compound containing no potassium i.e. the equi-molar mixture  $\text{Li}_2\text{SO}_4:\text{LiBr}$  alone, no transition to a high conducting phase was observed. The conductivity rose rapidly from  $10^{-6} \Omega^{-1}\text{cm}^{-1}$  at  $200^\circ\text{C}$ , but was always lower than the conductivity of the  $\text{K}^+$  ion-containing compound. This is illustrated in Fig. 1. DSC analysis presented a single broad peak at  $477^\circ\text{C}$  which may be related to the solid-melt, two-phase regions of this mixture described by Heed et al (9).

$\text{LiBr}$  alone has a conductivity of about  $3 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  at  $400^\circ\text{C}$  (8), or a factor of three below the binary mixture studied, and at this temperature,  $\text{K}_2\text{SO}_4$  is almost an insulator. It is, therefore, the  $\text{Li}_2\text{SO}_4$  lattice which remains conducting and the effect of the two additives is to reduce the  $\beta$ -phase to a lower temperature.

### CONCLUSIONS

It has been shown that the onset of the high conductivity  $\beta$ -phase of  $\text{Li}_2\text{SO}_4$  may be reduced from  $572^\circ\text{C}$  to  $324^\circ\text{C}$  by the incorporation of  $\text{LiBr}$  and small quantities of  $\text{K}_2\text{SO}_4$ . This new phase extends to the melting point of  $\text{Li}_2\text{SO}_4:\text{LiBr}:0.07 \text{K}_2\text{SO}_4$  ( $559^\circ\text{C}$ ) and is thus  $235^\circ$  long. At the transition, the conductivity is  $0.08 \Omega^{-1}\text{cm}^{-1}$ . In the high temperature range, the material is sufficiently conductive for it to be used in electrochemical cells; at room temperature, other compounds may be more useful.

### ACKNOWLEDGEMENT

Differential scanning calorimetric analysis of the materials by R. McMahon is gratefully acknowledged.



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